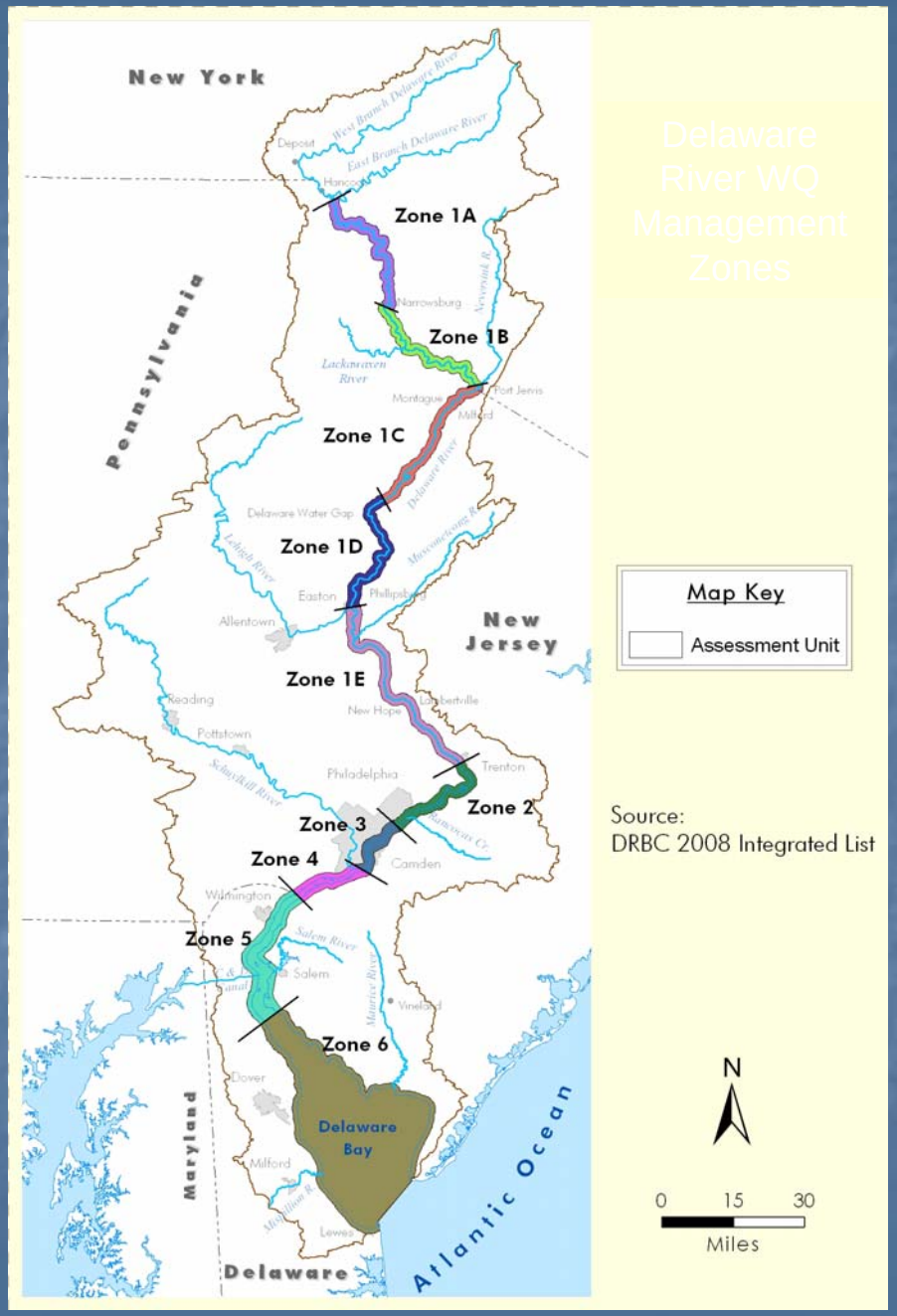
Ammonia Criteria for the Interstate Waters of the Delaware River

Toxics Criteria Subcommittee

May 14, 2009



Outline

1. Current DRBC Regulations re Ammonia
2. Technical Background
3. Comparison of Criteria: National versus State Standards
4. Ammonia Criteria Issues
5. Recommendations

Current DRBC Regulations

- Article 3 Water Quality Standards
  - **No** ambient or effluent requirements either basin-wide or for individual Zones.
  - Anti-degradation Existing Water Quality Parameters (Zones 1A to 1E):
    - Ammonia and Ammonium – means range between 15 to 41 µg/L from Hancock, NY to Delaware Water Gap.
    - Ammonia – medians range between <50 and 50 µg/L from Portland, PA to Trenton, NJ.

Current DRBC Regulations

- Article 4 Application of Standards
  - Section 4.30.5 – Other Substances in Effluents
    - In non-tidal waters, not to exceed a 30 day average of 20 mg/L as nitrogen.
    - In tidal waters, not to exceed a 30 day average of 35 mg/L as nitrogen.

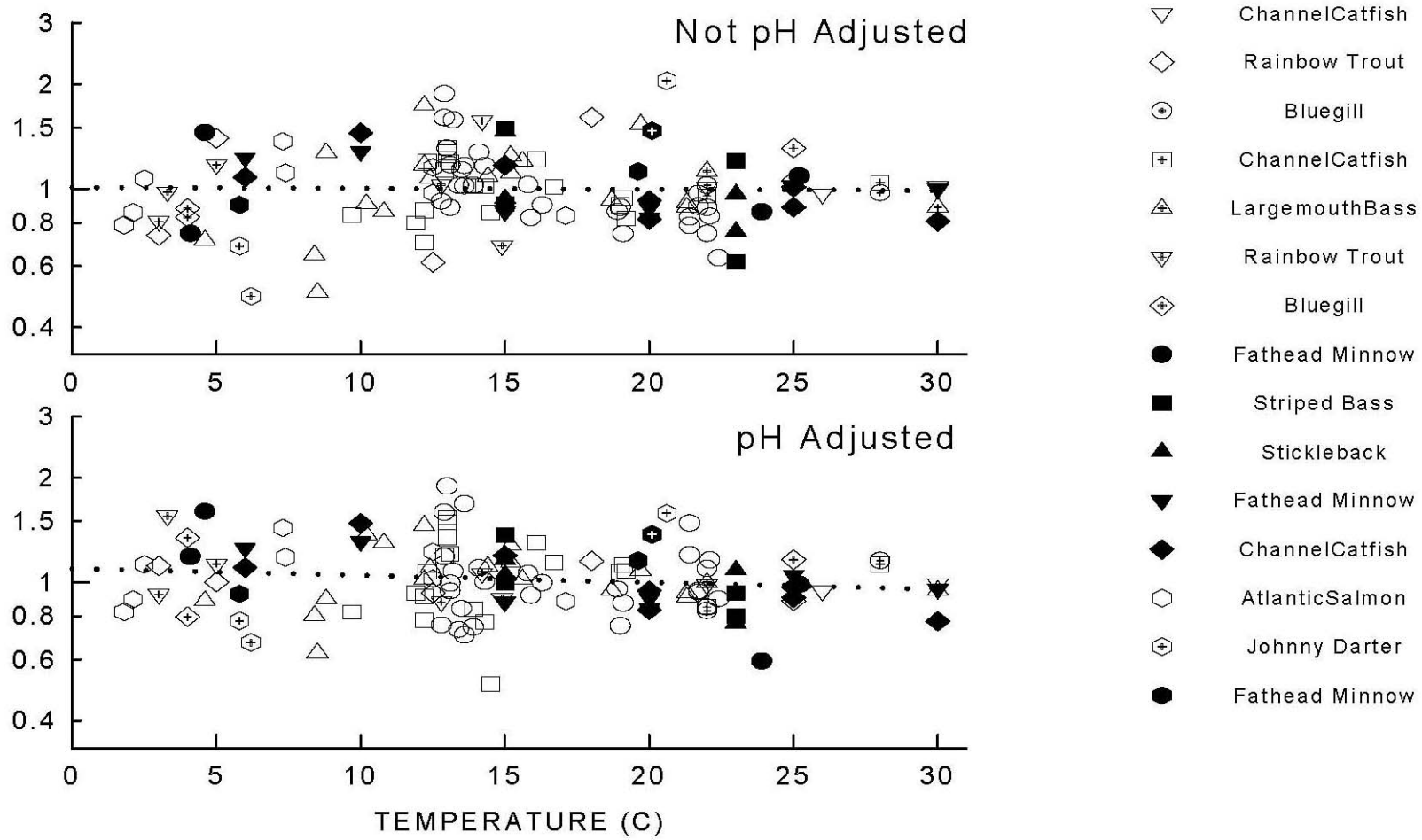
Technical Background

- Ammonia in aqueous solutions exists as two forms:
  - NH_3 or un-ionized ammonia, and
  - NH_4^+ - ammonium ion
  - The proportion of each depends on the pH and equilibrium constant pK which is dependent on temperature.
- Ammonia speciation also depends on ionic strength, but in freshwater, this effect is much smaller than pH and temperature and was not considered in developing the criteria.

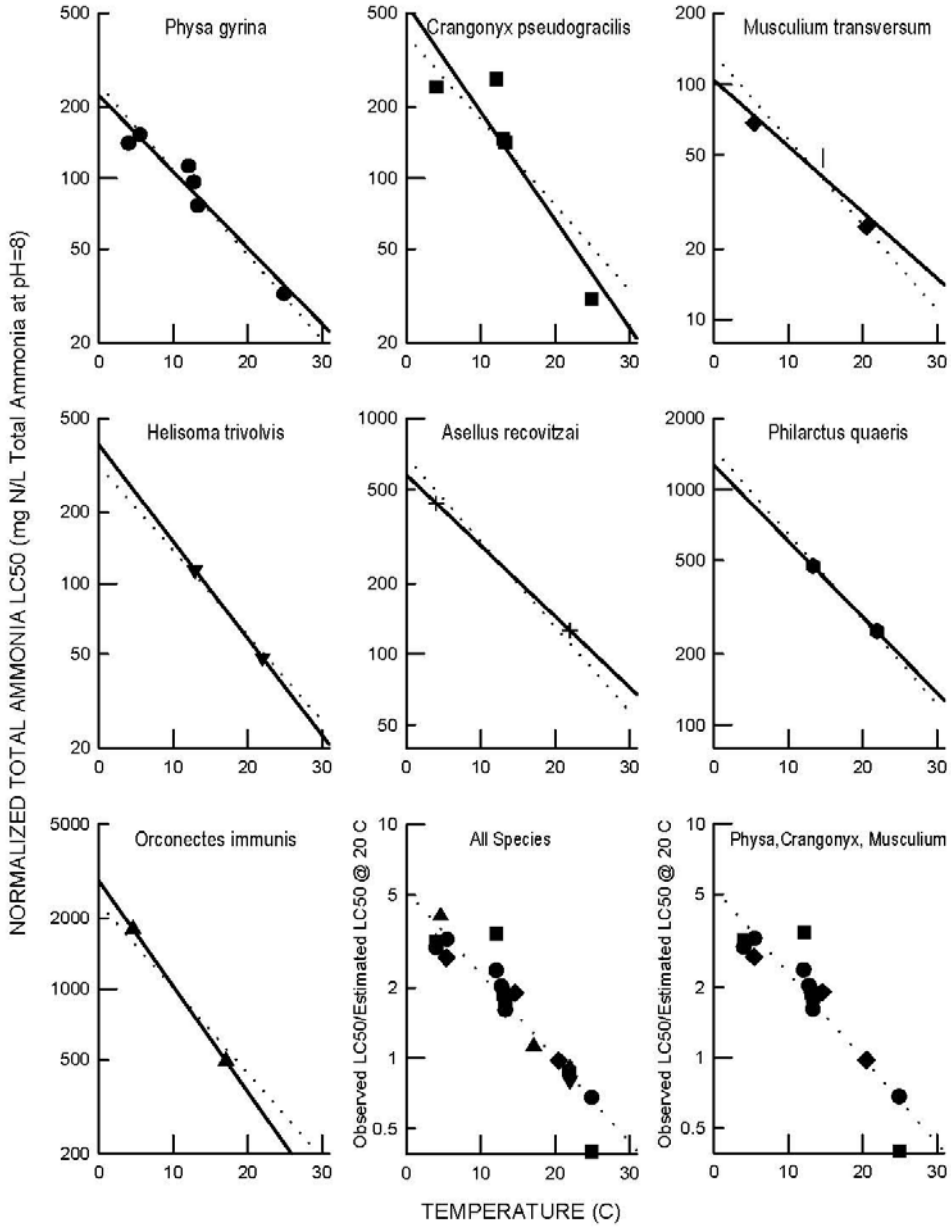
Technical Background

- pH Dependence
  - Considerable evidence indicates that the effects of pH on ammonia toxicity is due to the joint toxicity of un-ionized ammonia and the ammonium ion.
  - At very high and low pHs, pH can affect membrane function and other physiological processes that could alter ammonia toxicity.
- Temperature Dependence
  - The effect of temperature on the joint toxicity of ammonia is not strongly indicative of joint toxicity, and was therefore not used to adjust the acute criterion. However, invertebrate acute toxicity does decrease at lower temperatures.

Figure 4. The effect of temperature on normalized acute ammonia toxicity in terms of total ammonia. Data were normalized by dividing measured LC50s by regression estimates of LC50s at 20°C for individual datasets for Figure 2 (top plot) and Figure 3 (bottom plot).



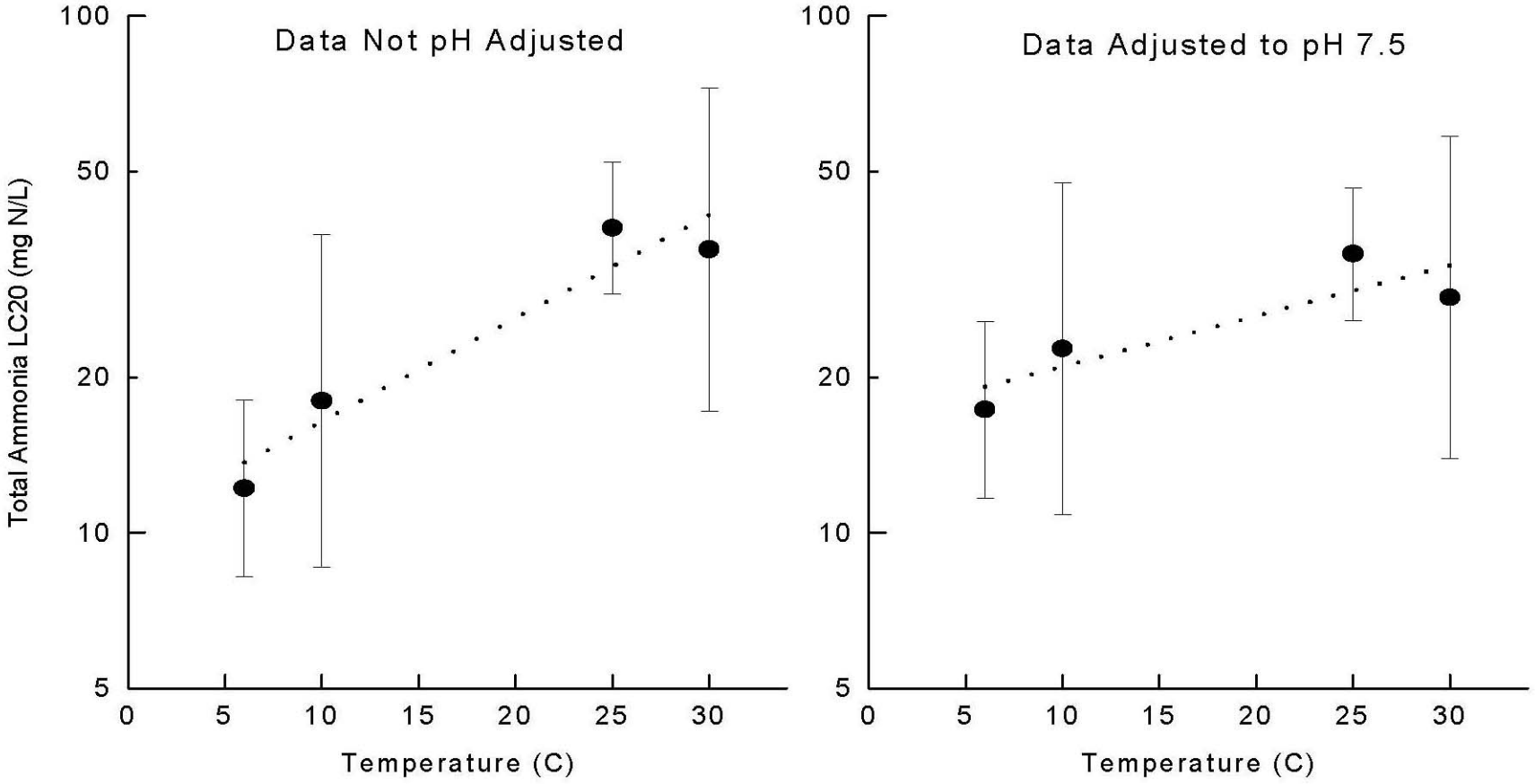
Temperature Dependence of Acute Ammonia Toxicity
to Invertebrate Organisms from Arthur et al. (1987).
(Solid line denotes species slope; Dotted line denotes pooled slope)



Technical Background

- Temperature Dependence (cont.)
  - There is little data on the relationship of temperature to chronic toxicity in fish, and no data on the relationship in invertebrates.
  - Data that is available shows the opposite relationship to temperature compared to acute toxicity (i.e., toxicity is greater at lower temperatures for chronic toxicity.
  - Because the most sensitive species for chronic effects is the amphipod *Hyalella*, the chronic criterion will vary according to the invertebrate chronic toxicity : temperature relationship.

Figure 5. The effect of temperature on chronic ammonia lethality to fathead minnows in terms of total ammonia (DeGraeve et al. 1987). Symbols denote LC20s and 95% confidence limits and lines denote linear regressions of log LC versus temperature. Figure on left is for estimated LC50s at test pH and figure on right is for LC50s adjusted to pH=7.5 based on pooled relationship of chronic toxicity to pH.



Federal/State Acute Criteria Comparisons

Agency	Class	Criteria (mg/L)	Value at pH=7.5
U.S. EPA	Salmonids Present	$CMC = 0.275/1+10^{(7.204-pH)} + 39.0/1+10^{(pH-7.204)}$	13.3
	Salmonids Not Present	$CMC = 0.411/1+ 10^{(7.204-pH)} + 58.4/1+10^{(pH-7.204)}$	19.9
DE	Salmonids Present	$CMC = 0.275/1+10^{(7.204-pH)} + 39.0/1+10^{(pH-7.204)}$	13.3
	Salmonids Not Present	$CMC = 0.411/1+ 10^{(7.204-pH)} + 58.4/1+10^{(pH-7.204)}$	19.9

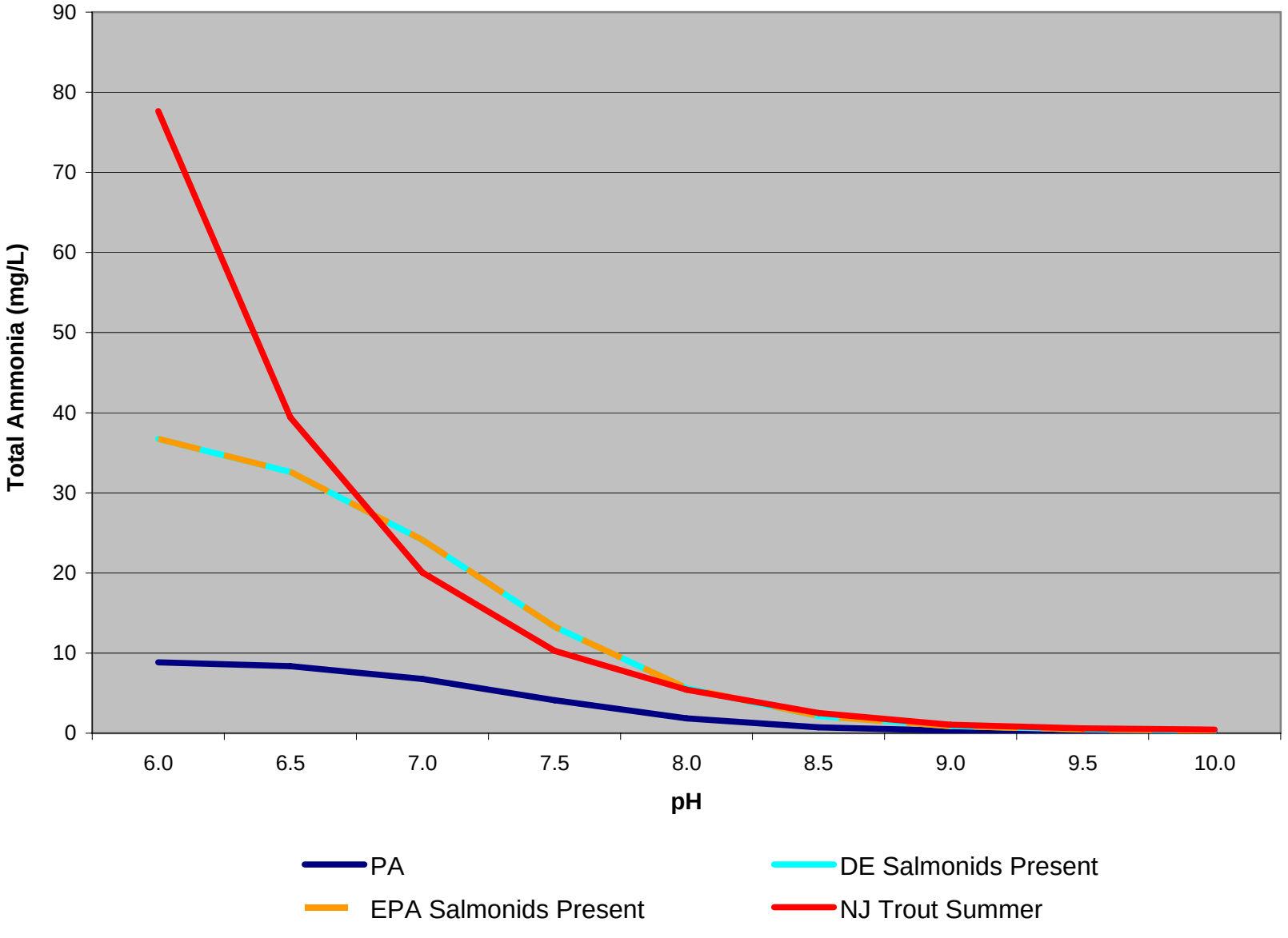
Federal/State Acute Criteria Comparisons

Agency	Class	Criteria (mg/L)	Value at Temp=20
NJ (un-ionized)	Trout pH < 8.3	$0.179*10^{0.026*(Temp-20)+0.41*(pH-7.8)}$	10.9 (pH=7.5)
	Trout pH ≥ 8.3	$0.179*10^{(0.026*(Temp-20)+0.20)}$	2.5 (pH=8.5)
	Non-Trout Summer pH < 8.3	$0.201*10^{0.026*(Temp-20)+0.41*(pH-7.8)}$	12.2 (pH=7.5)
	Non-Trout Summer pH ≥ 8.3	$0.201*10^{0.026*(Temp-20)\ +\ 0.20)}$	2.9 (pH=8.5)

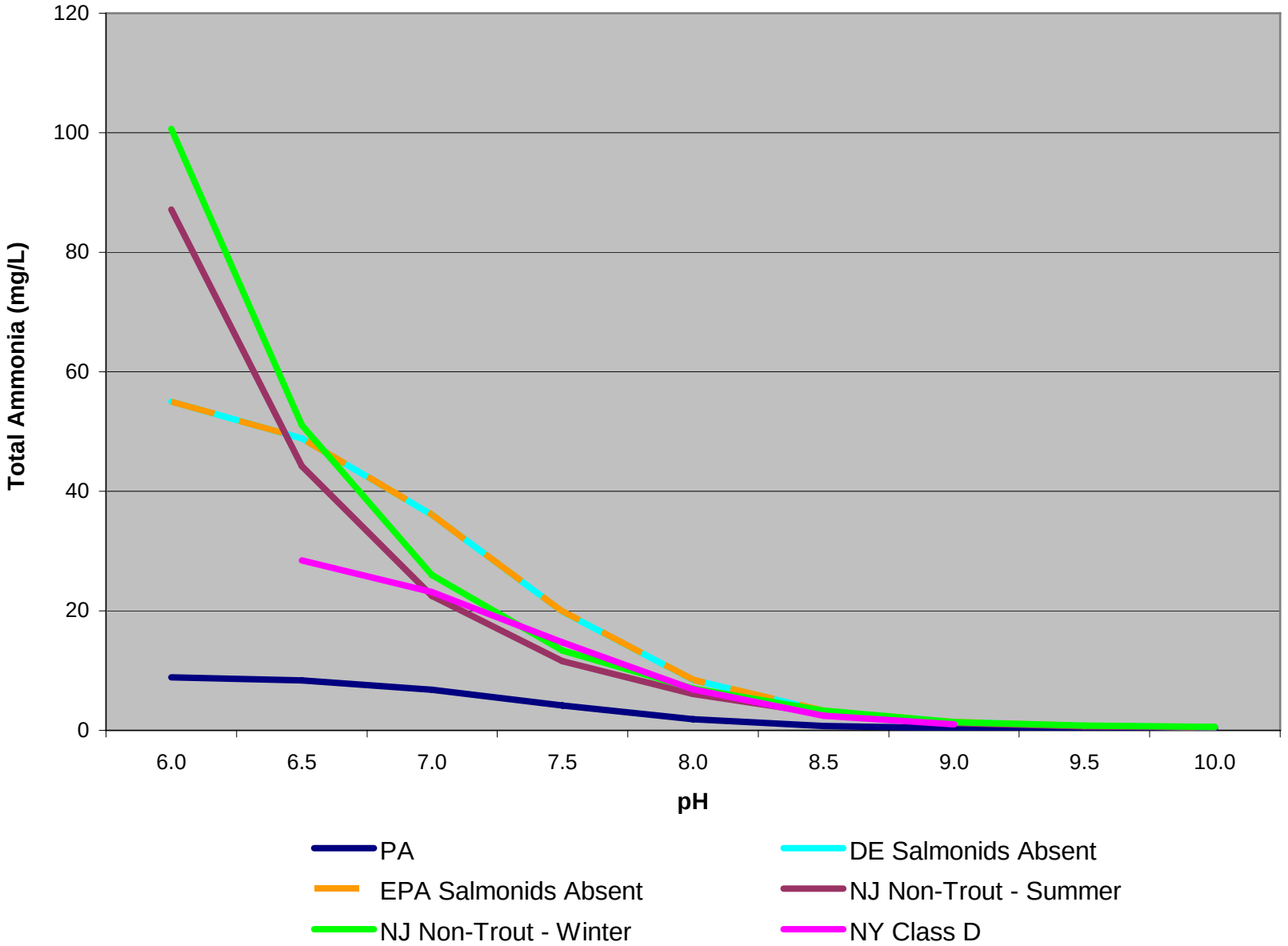
Federal/State Acute Criteria Comparisons

Agency	Class	Criteria	Value at pH=7.5, Temp=20
NJ **(un-ionized)**	Non-Trout Winter pH < 8.3	$0.232*10^{(0.026*(Temp-20) + 0.41*(pH-7.8))}$	14.1 **(pH=7.5)**
	Non-Trout Winter pH ≥ 8.3	$0.232*10^{(0.026*(Temp-20) + 0.41*(pH-7.8))}$	3.3 **(pH=8.5)**
PA **(Total)**	All	$(\text{un-ionized-}NH_{3)} * \log^{-1} (pKt - pH) + 1$	5.9 **(pH=7.5)**
NY **(un-ionized)**	Class D only	Tables relating standard to pH & temperature; Class D only	0.18 **(pH=7.5)**

Comparison of Ammonia Criteria Values at 25 C
PA Maximum Criteria vs EPA/DE/NJ Acute Criteria
Trout



Comparison of Ammonia Criteria Values at 25 C
PA Maximum Criteria vs EPA/DE/NJ Acute Criteria
Non-Trout



Federal/State Chronic Criteria Comparisons

Agency	Class	Criteria	Value at Temp=20
U.S. EPA	Fish Early Life Stages Present	$CCC = 0.0577/1 + 10^{(7.688-pH)} + 2.487/1+10^{(pH-7.688)} * Min(2.85, 1.45*10^{0.028(25-T)})$	4.3 **(pH=7.5)**
	Fish Early Life Stages Absent	$CCC = 0.0577/1 + 10^{(7.688-pH)} + 2.487/1+10^{(pH-7.688)} * 1.45*10^{0.028(25-MAX(T,7))}$	8.0 **(pH=7.5)**
DE	Fish Early Life Stages Present	$CCC = 0.0577/1 + 10^{(7.688-pH)} + 2.487/1+10^{(pH-7.688)} * Min(2.85, 1.45*10^{0.028(25-T)})$	4.3 **(pH=7.5)**
	Fish Early Life Stages Absent	$CCC = 0.0577/1 + 10^{(7.688-pH)} + 2.487/1+10^{(pH-7.688)} * 1.45*10^{0.028(25-MAX(T,7))}$	8.0 **(pH=7.5)**

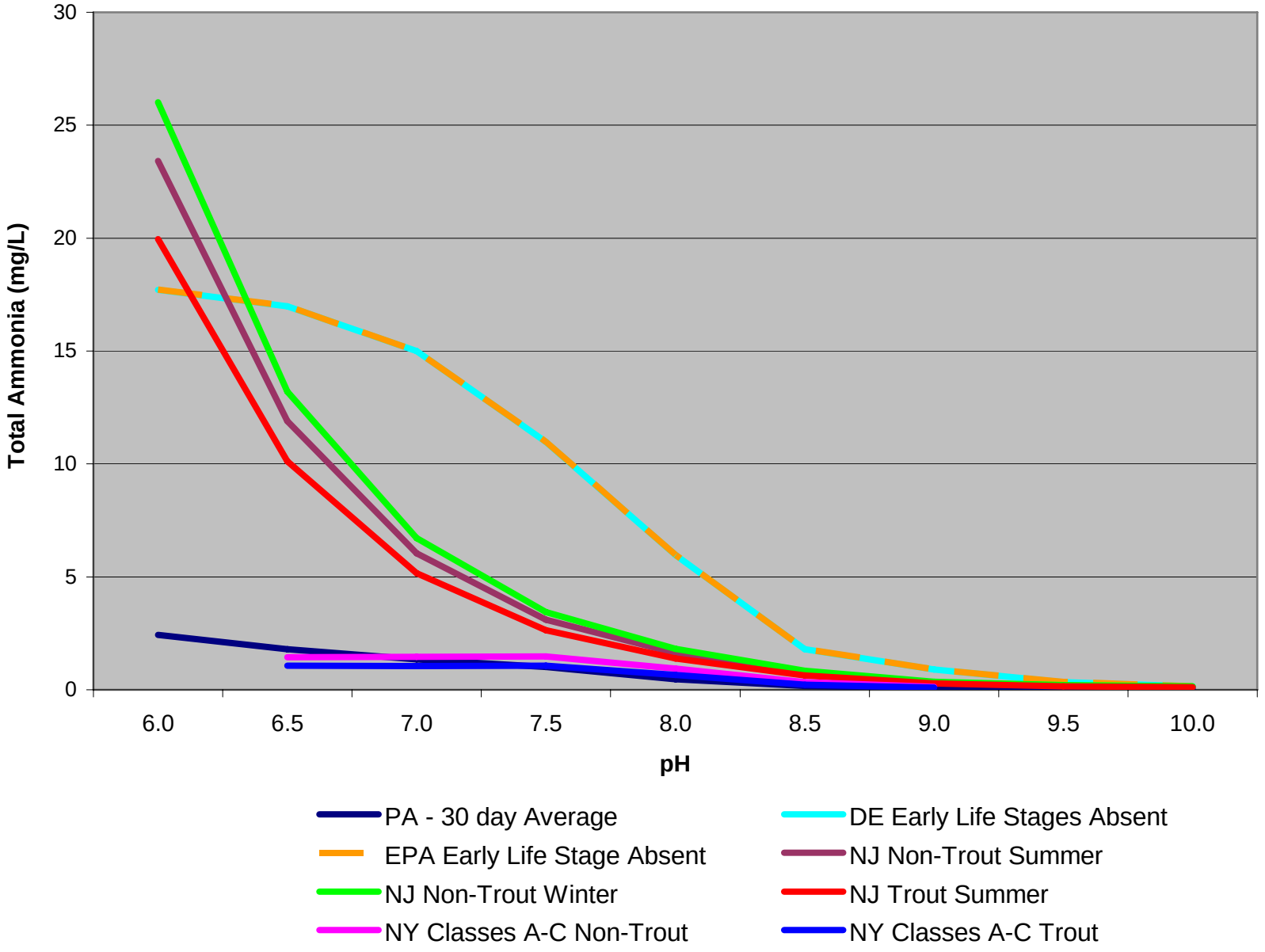
Federal/State Chronic Criteria Comparisons

Agency	Class	Criteria	Value at Temp=20
NJ **(un-ionized)**	Trout pH < 8.3	$0.046*10^{0.026*(Temp-20)+0.41*(pH-7.8)}$	2.8 **(pH=7.5)**
	Trout pH ≥ 8.3	$0.046*10^{(0.026*(Temp-20)+0.20)}$	0.7 **(pH=8.5)**
	Non-Trout Summer pH < 8.3	$0.054*10^{0.026*(Temp-20)+0.41*(pH-7.8)}$	3.3 **(pH=7.5)**
	Non-Trout Summer pH ≥ 8.3	$0.054*10^{0.026*(Temp-20)\ +\ 0.20)}$	2.9 **(pH=8.5)**
	Non-Trout Winter pH < 8.3	$0.060*10^{0.026*(Temp-20)\ +\ 0.41*(pH-7.8)}$	6.7 **(pH=7.5)**

Federal/State Chronic Criteria Comparisons

Agency	Class	Criteria	Value at Temp=20
NJ **(un-ionized)**	Non-Trout Winter pH ≥ 8.3	$0.060*10^{0.026*(Temp-20) + 0.41*(pH-7.8)}$	0.9 **(pH=8.5)**
PA **(Total)**	All	(un-ionized-$NH_{3)}$ * $\log^{-1}$ (pKt – pH) + 1	1.4 **(pH=7.5)**
NY **(un-ionized)**	Trout & Trout Spawning, Classes A-C	Tables relating standard to pH & temperature	0.019 **(pH=7.5)**
	Non-Trout, Classes A-C	Tables relating standard to pH & temperature	0.026 (pH=7.5)

Comparison of Ammonia Criteria Values at 25 C
PA 30 Day Average Criteria vs EPA/DE/NJ Chronic Criteria



Ammonia Criteria Issues

- Need uniform criteria for shared waters.
  - Significant differences between state criteria in shared waters.
  - Differing criteria hampers cumulative assessment of multiple discharges.
- Form of the Criteria

  Total vs Un-ionized
  - EPA, DE and PA recommend total ammonia.
  - NJ and NY recommend un-ionized ammonia.

Ammonia Criteria Issues

- For chronic criteria, how would the early life stage criteria be implemented if this option is selected? By season, specified period of time?
- Application of criteria:
  - pH data or value to be used.
  - Temperature data or value to be used.
  - Duration of criteria:
    - 1 hour versus 3 hour for acute criteria
    - 4 days versus 30 days for chronic criteria
  - Design flows

Recommendations

- Acute Criteria:
  - Adopt EPA recommended criteria formulas for total ammonia.
  - These criteria are similar to NJ at pH>7.0, but much less protective than PA.
  - Criteria are related to pH, but not to temperature.
  - Salmonids present criteria would apply only to Zone 1A where maintenance and propagation of trout are a designated use.
  - Salmonids absent criteria would apply in Zones 1B through 1E, 2 through 6.

Recommendations

- Chronic Criteria:
  - Adopt EPA recommended criteria formulas for total ammonia.
  - These criteria are similar to the other states at pH>8.5. Less restrictive than NJ at pH>6.5, and less restrictive than PA at pH>6.0.
  - Criteria are related to both pH and temperature.
  - Criteria are not related to the presence of Salmonids, but are related to the presence of early life stages.

Recommendations

- Chronic Criteria (cont.):
  - Both criteria formulas would apply in Zones 1A through 1E, 2, part of Zone 5, and 6.
  - Criterion for early life stages absent would apply in Zones 3, 4, and upper Zone 5.
  - Options for selecting criterion formula based on presence of early life stages:
    - Adopt formulas and implement on a site-specific basis (allows for seasonal criteria).
    - Specify period when each criterion formula would apply (e.g., March thru October period for early life stage present criterion)

Recommendations

- Application of Standards:
  - Duration – Follow EPA recommendations and use 1 hour for acute criteria and 30 days for chronic criteria. This recommendation is more stringent than NJ, less stringent than PA that applies criterion as a maximum, and the same as DE and NY?.
  - pH and temperature values – options are:
    - Utilize site-specific data typically from automatic monitors (for all or specified Zones).
    - Specify a median pH value of 7.1 (Section 4.20.5A3.) and background temperature specified in Section 4.30.6C.1. for Zones 2, 3 and 4.

Recommendations

- Application of Standards:
  - pH and temperature values – options are:
    - Specify median pH values for Existing Water Quality (EWQ) at Interstate Control Points (ICPs) in Special Protection Waters in Zones 1A-1E [Section 3.10.3A.2.g.3)].
  - Design Flows:
    - Acute Criteria – 2500 cfs at Trenton and 7Q10 for other tributaries.
    - Chronic Criteria – 30Q3 flow at both Trenton and for other tributaries.

Marine Criteria for Ammonia

- Only three of the five signatory parties have water quality criteria for un-ionized ammonia. PA and DE do not have criteria.
- EPA and NY have the same criteria. NJ's criteria are somewhat lower.
- Total ammonia criteria vary depending on the pH, temperature and salinity. U.S. EPA (1989) provides conversion tables. Total ammonia criteria are lower at higher salinities.

Federal/State Marine Criteria Comparisons

Agency	Class	Acute	Chronic
U.S. EPA (un-ionized)		0.233	0.035
DE	-	-	-
NJ (un-ionized)	SE	0.115	0.030
	SC	0.094	0.024
PA	-	-	-
NY (un-ionized)	SA, SB, SC, I, SD	0.23	-
	SA, SB, SC, I	-	0.035

Recommendations

- Determine the basis for the differences between NJ's and national criteria.
- Continue discussion of appropriate criteria at the next meeting of the subcommittee.